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(54) **Lead-free high performance gasoline.**

(57) A lead-free high performance gasoline whose characteristics are within the extent of the standards for racing car gasoline and which can easily cope with annual slight changes in the standards.

Particularly, this invention provides a lead-free high performance gasoline which contains (1) toluene in an amount of from 50 to 70% by volume, n-heptane in an amount of from 2 to 10% by volume, isopentane in an amount of from 5 to 25% by volume and, if necessary, direct distillation light naphtha in an amount of from 10 to 30% by volume and a C₄ fraction of distillate in an amount of from 2 to 5% by volume or (2) toluene in an amount of from 45 to 60% by volume, methyl-tert-butyl ether in an amount of from 10 to 20% by volume, n-heptane in an amount of from 10 to 20% by volume, isopentane in an amount of from 5 to 15% by volume and a C₄ fraction of distillate in an amount of from 2 to 5% by volume, wherein the lead-free high performance gasoline satisfies the conditions of: density at 15°C ≤ 0.81 g/cm³; 97 < research octane number ≤ 101 ; and Reid vapor pressure ≥ 0.4 kg/cm².

By changing blending ratio of each component in the above composition (1) or (2) within the above range, the gasoline of this invention can easily cope with annual changes in the fuel standards for rallies and races without reducing output characteristics.

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FIELD OF THE INVENTION

This invention relates to lead-free high performance gasoline, especially a lead-free high performance gasoline whose characteristics are within the extent of the application of the standard for racing car gasoline.

More particularly, it relates to a lead-free high performance gasoline which contains specified amounts of specified base materials such as toluene and the like and has certain defined properties.

BACKGROUND OF THE INVENTION

Motor sports are becoming widely popular in recent years in Japan, with frequent international auto races held within the country, as well as the increasing number of home team entrants for international races outside the country. Properties of fuels to be used in these international races are standardized for each type of races by the Federation of International Automobile (FIA). In consequence, auto race entrants have to design a gasoline formulation which can satisfy such property standards and is able to maximize engine power.

Properties of gasoline are also standardized for formula races such as Formula One (F1) which is regarded as the greatest circuit race in the world, and not only the quality of fuel but also its amount to be used are restricted in many cases. Because of this, it is important to improve not only maximum engine power but also fuel consumption when gasoline formulation is designed. For example, fuel consumption has become an important factor in the F1 race held in 1988 because fuel tank capacity was restricted to 150 liters. With the aim of overcoming this problem, Honda R & D Co., Ltd. has developed a gasoline formulation which was excellent in both engine power and fuel consumption (cf. a teaching material (No. 900-72) used in the meeting held by The Japan Society of Mechanical Engineers ('90-11/1-2)).

While specially designed engines are used in formula races such as F1, remodeled stock engines are used in other auto races including rallies such as WRC (World Rally Championship) and the like and general circuit races such as SWC (Sports car World Championship), JSPC (Japan Sports Prototype car Championship) and the like. In the case of these engines for rally and circuit race use, fuel standards and engine characteristics are different from those in the specially designed engines for formula race use. In consequence, it is important to design gasoline formulations suitable for use in these rally and general circuit race engines. In the field of these rallies and general circuit races, efforts for increasing engine power have been made mainly through the remodeling of stock engines. Virtually nothing is known about such efforts made through studies on the improvement of gasoline formulation.

SUMMARY OF THE INVENTION

In view of the above, it therefore becomes an object of the present invention to provide a lead-free high performance gasoline whose characteristics are within the extent of the application of the standard for racing car gasoline.

Particularly, in accordance with the present invention, there is provided a lead-free high performance gasoline which contains

(1) toluene in an amount of from 50 to 70% by volume, n-heptane in an amount of from 2 to 10% by volume, isopentane in an amount of from 5 to 25% by volume and, if necessary, direct distillation light naphtha in an amount of from 10 to 30% by volume and a C₄ fraction of distillate in an amount of from 2 to 5% by volume or

(2) toluene in an amount of from 45 to 60% by volume, methyl-tert-butyl ether in an amount of from 10 to 20% by volume, n-heptane in an amount of from 10 to 20% by volume, isopentane in an amount of from 5 to 15% by volume and a C₄ fraction of distillate in an amount of from 2 to 5% by volume, the lead-free high performance gasoline also satisfying the conditions of density at 15°C ≤ 0.81 g/cm³, 97 < research octane number ≤ 101 and Reid vapor pressure ≥ 0.4 kg/cm².

Other objects and advantages of the present invention will be made apparent as the description progresses.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing, the single figure is a graph showing performance of gasoline compositions in accordance with first and second aspects of the present invention in which (A) shows performance in relation to spark ignition advance and (B) shows performance in relation to output torque.

DETAILED DESCRIPTION OF THE INVENTION

The inventors of the present invention have conducted intensive studies, with the aim of developing a high power gasoline which satisfies regulations of the Item J of FiSA (a subordinate organization of FIA) for racing cars to be used in rallies such as WRC and the like or general circuit races such as SWC, JSPC and the like. To develop such a gasoline fuel, the following points were taken into consideration: (1) the gasoline product should be free from lead, (2) it should be composed of low priced components which can be supplied in sufficient amounts, (3) it should be possessed of excellent startability and (4) it should be capable of advancing ignition timing within medium and high speed ranges, thereby improving spark ignition advance and enabling sharp increase in the output torque and power.

As it is well known, the term "spark ignition advance" described in the above point (4) is used to express a crank angle at the time of ignition in advance of the top dead center whose crank angle is defined as 0°. For example, an expression "10° spark advance of ignition" means ignition at 10° crank angle in advance of the top dead center. The spark ignition advance has a critical value for obtaining maximum torque and power, because too much advance in the ignition timing causes increase in the compression work and generation of knocking due to increased combustion pressure and temperature. Since every engine is used under high speed and high load working conditions during the most part of traveling in the case of a rally and the like, efforts are made to obtain a high power by excluding the aforementioned negative factors. The main purpose of the aforementioned point (4) is to develop a gasoline composition which can further advance the critical spark ignition advance value of conventional gasoline so that output torque and power are improved as the results.

Another important point of the present invention is to design a gasoline formulation which satisfies the fuel property regulations of the Item J of the FiSA and, at the same time, can cope with the annually proposed slight changes in the fuel standard. For example, the upper limit of the research octane number (RON) of lead-free type gasoline is 99 for the year of 1991, but is planned to be increase to 100 in 1992. Since each composition of the gasoline formulation of the present invention has such a flexible blending range that the inventive gasoline can cope with these annual changes in the fuel standard without reducing the output properties.

A first aspect of the gasoline of the present invention is described in the following.

Toluene is a base material of the gasoline of the present invention. Amounts of the base material if too large would result in correlatively too small amounts of other components to be blended, thus rendering impossible to obtain necessary properties within the aforementioned ranges and also causing extreme difficulty in changing the amount of each component to cope with the annual changes in the fuel standard. Amounts of the base material if too small would also render impossible to obtain necessary properties within the aforementioned ranges, thus causing difficulty in sharply improving output torque and power. In consequence, toluene may be used in the gasoline formulation in an approximate amount of from 50 to 70% by volume.

Toluene to be used in the gasoline of the present invention may be obtained for example from catalytically reformed gasoline or cracking gasoline which is a by-product formed during ethylene production, by subjecting the gasoline material to a solvent extraction method such as sulfolane technique, Udex process or the like. In this instance, the term "catalytically reformed gasoline" means a gasoline fraction prepared from heavy naphtha or the like by the commonly known catalytic reforming process (contact catalysis treatment using a reforming catalyst under pressurized high temperature conditions). A toluene preparation obtained by such means will have a purity of about 97% by volume or more.

Normal heptane which has an octane number of zero is an essential component for use in the octane number adjustment of the gasoline of the present invention. According to the present invention, the octane number becomes too high when the gasoline is composed solely of the aforementioned base material (that is, 100% by volume of toluene). In order to reduce and adjust octane number of the gasoline to the aforementioned level ($97 < \text{RON} \leq 101$) keeping the amount of toluene within the aforementioned range, normal heptane having an octane number of zero may be used most effectively on the basis of the following reason. That is, though the octane number can be reduced by changing the amount of isopentane or the like as another component of the gasoline of the present invention, it is necessary to use a large volume of isopentane to control the octane number within the aforementioned RON range, thus rendering impossible to adjust contents of other components including toluene within their predetermined ranges.

Normal heptane may be used in such an amount that the RON value of the resulting gasoline is controlled within the aforementioned range. Amounts of normal heptane if too small would bear no significant effect in reducing octane number, and if too large would entail too low octane number which is smaller than the desired RON range. In consequence, normal heptane may be used in an approximate

amount of from 2 to 10% by volume.

Normal heptane to be used in the gasoline of the present invention may be obtained for example by subjecting naphtha fraction of crude oil, preferably desulfurized naphtha, to precise fractional distillation or molecular sieve fractionation. A normal heptane preparation obtained by such means will have a purity of about 97% by volume or more.

Isopentane is another basic component of the gasoline of the present invention, which is blended mainly for the purpose of reducing and controlling density of the gasoline product and is also useful in controlling octane number.

Isopentane may be used in such an amount that density of the resulting gasoline is controlled within the range described in the foregoing. Amounts of isopentane if too small would bear no significant effect in reducing density, and if too large would entail too low density value which is smaller than the desired density range. In consequence, isopentane may be used in an approximate amount of from 5 to 25% by volume.

Isopentane to be used in the gasoline of the present invention may be obtained for example by subjecting light naphtha, preferably desulfurized light naphtha, reformat, isomerate or the like to precise fractional distillation. In this instance, the term "isomerate" means a fraction of distillate having a boiling point of from 25 to 85°C, which is obtained by isomerizing a pentane fraction, a hexane fraction or a mixture thereof as a raw material prepared from naphtha, natural gasoline, direct distillation gasoline, reformat or the like, more illustratively by converting straight-chain paraffinic hydrocarbons into side chain-containing isomers without changing chemical compositions. Such isomerization reaction may be effected for example by general isomerization processes such as Shell isomerization process and the like or by hydrogen isomerization processes such as Penex process, Hysomer process and the like. An isopentane preparation obtained by such means will have a purity of about 97% by volume or more.

Direct distillation light naphtha is a multi-component distillate which is composed mainly of paraffinic components and naphthenic components. This type of naphtha is used as an optional component in the gasoline of the present invention for the purpose of keeping startability of an engine and combustibility of the gasoline in good conditions through improvement the distillation properties of the gasoline. In some cases, excellent startability of an engine and excellent combustibility of the inventive gasoline can be obtained without blending the direct distillation light naphtha depending on the type, operation conditions, operation environment and the like of the engine. In that case, blending of the direct distillation light naphtha may not be required.

When required, direct distillation light naphtha may be used in an approximate amount of from 10 to 30% by volume. Amounts of direct distillation light naphtha if too small would bear no significant effect in improving engine startability and gasoline combustibility, and if too large would produce no proportionally greater effect but rather cause decrease in the output torque and the like. Since direct distillation light naphtha has functions to decrease density and reduce octane number in some degree, the amount of isopentane described above may be reduced to a level of about 5 to 15% by volume when direct distillation light naphtha is blended.

The direct distillation light naphtha, composing mainly of paraffinic components and naphthenic components, is obtained by atmospheric distillation of crude oil and has an initial boiling point of about 20 to 50°C and a final boiling point of about 70 to 120°C.

The C₄ fraction of distillate is used in the gasoline of the present invention for the purpose of maintaining volatility of the gasoline at a certain level and keeping startability of an engine in good condition. Amounts of the C₄ fraction of distillate if too small would bear no significant effect in improving such an engine startability, and if too large would produce no proportionally greater effect but rather induce a so-called "vapor lock" phenomenon which is a state of poor fuel supply condition caused by the formation of bubbles in the supply line of fuel to an engine. In consequence, the C₄ fraction may be used in an approximate amount of from 2 to 5% by volume.

Examples of the C₄ fraction of distillate to be used in the gasoline of the present invention include distillation fractions containing butane, butene and the like as the main components, which are obtained at the time of atmospheric distillation of crude oil, production of reformat or production of cracking gasoline.

The gasoline of the present invention which comprises the aforementioned components satisfies the conditions of: density (15°C) ≤ 0.81 g/cm³; $97 < \text{RON} \leq 101$; and Reid vapor pressure (RVP) ≥ 0.4 kg/cm². When these conditions are satisfied, the inventive gasoline can be used in various rallies and general circuit races as an engine fuel which satisfies the fuel standards, and, even when these fuel standards are changed slightly in every year, the inventive gasoline can cope easily with these changes by changing blending amounts of the aforementioned components within the aforementioned ranges. In this instance, the density at 15°C, the RON value and the RVP value described above are measured in accordance with the methods

of JIS K2249, JIS K2280 and JIS K2258, respectively.

In addition, the gasoline of the present invention which comprises the aforementioned components and has the aforementioned properties satisfies the conditions of: lead contents \leq about 0.013 g/l; oxygen contents \leq about 3.7% by weight; and benzene contents \leq about 5% by volume. When upper limit of lead contents is around the just described level, the gasoline can be regarded safely as lead-free. When upper limits of oxygen and benzene contents are respectively around the just described levels, the inventive gasoline can be used in various rallies and general circuit races as an engine fuel which satisfies the fuel standards, and, even when these fuel standards are changed slightly in every year, the inventive gasoline can cope easily with these changes by changing blending amounts of the aforementioned components within the aforementioned ranges. In this instance, the lead content is measured in accordance with the methods of JIS K2255.

Next, a second aspect of the gasoline of the present invention is described.

Except for the additional use of methyl-tertbutyl ether (MTBE), composition of the gasoline of the second aspect of the present invention is basically the same as that of the first aspect gasoline, but with slight difference in the blending ratio of each component. The following describes these differences in detail.

MTBE is now regarded as a noteworthy base material in Japan, because it has a high octane number and is a relatively light fraction of distillate. Since MTBE is an oxygen-containing organic compound, its blending ratio is restricted to a certain level by the fuel standards in various rallies and general circuit races, while its blending effect is obtained only when the blending ratio is increased to a certain level because of its hydrocarbon-like nature. In consequence, in the gasoline of the present invention, MTBE may be used in an approximate amount of from 10 to 20% by volume.

MTBE to be used in the gasoline of the present invention may be produced for example by reacting methanol with isobutene in the presence of an acid catalyst. Such a type of production processes have been reported for example by Chemische Werke Huls AG in Germany, Snamprogetti in Italy, Gulf Canada in Canada, ARCO Technology in U.S.A. and Mitsui Toatsu Chemicals, Inc. in Japan. An MTBE preparation obtained by such means will have a purity of about 97% by volume or more.

Since MTBE also functions as a base material in the gasoline of the present invention as described above, the blending amount of toluene can be reduced to such a level that the reduced portion is supplemented with desired amount of MTBE. In consequence, in the gasoline of the second aspect of the present invention, toluene may be used in an approximate amount of from 45 to 60% by volume.

As described in the foregoing, MTBE has a high octane number while normal heptane has a function to reduce octane number of the inventive gasoline. In consequence, blending amount of normal heptane in the gasoline of the second aspect of the present invention may be increased to a higher level than the case of the first aspect gasoline. Illustratively, normal heptane may be used in an approximate amount of from 10 to 20% by volume.

Isopentane and the C_4 fraction may be used basically in the same amounts as those in the gasoline of the first aspect of the present invention. According to the gasoline of the second aspect of the present invention, direct distillation light naphtha is not required because startability of an engine and combustibility of the gasoline can be improved by the use of MTBE, though the presence of the light naphtha does not spoil nature of the inventive gasoline.

Properties of the gasoline of the second aspect of the present invention, that is, density at 15°C, RON and RVP, as well as contents of lead, oxygen and benzene in the gasoline, may be the same as those of the first aspect gasoline.

If necessary, the gasoline of the present invention may be further supplemented with known fuel oil additives which include for example: oxidation inhibitors such as amine-based antioxidants, phenolic antioxidants and the like; metal deactivators such as thioamide-type compounds and the like; surface ignition inhibitors such as organic phosphorous compounds and the like; detergent-dispersants such as succinic acid imide, polyalkyl amine, polyether amine and the like; deicing agents such as polyhydric alcohols, ethers thereof and the like; combustion improvers such as alkali metal salts and alkaline earth metal salts of organic acids, sulfuric acid esters of higher alcohols and the like; antistatic agents such as ampholytic surface active agents and the like; and coloring agents such as azo dyes and the like. These fuel oil additive agents may be used alone or as a mixture of two or more. They may be used in optional amounts, but preferably in a total amount of 0.1% by weight or less.

As has been described in detail in the foregoing, in accordance with the gasoline of the present invention, ignition timing can be advanced sharply without generating knocking within the range of frequent speeds of engines for use in various rallies and general circuit races, thereby rendering possible sharp increase in the output torque and power. Also, according to the gasoline of the present invention, even when

fuel standards for the aforementioned various rallies and general circuit races are changed in every year, the inventive gasoline can cope easily with such an alteration by slightly changing blending amounts of the gasoline components. Because of these effects, the gasoline of the present invention is markedly useful as gasoline for racing car use.

EXAMPLES

The following inventive and comparative examples are provided to further illustrate the present invention. It is to be understood, however, that the examples are for purpose of illustration only and are not intended as a definition of the limits of the invention.

Gasolines in accordance with the first and second aspects of the present invention were formulated within the limits of the fuel standard provided by the Item J of the FiA for the year of 1990. Compositions and properties of the thus prepared two gasolines are shown in Table 1 as inventive examples 1 and 2.

As a comparative example, a gasoline composition was prepared in which RON value was set within the fuel standard (99.0 or less), while MON which contributes to high speed antiknock property was set to its maximum value by blending paraffinic components (alkylate, isooctane and isopentane) to maximize high speed antiknock property. Composition and properties of the comparative example gasoline are also shown in Table 1.

TABLE 1

	Inventive 1	Example 2	Comparative Example
Components			
Toluene	62	52	10
MTBE	-	20	-
Normal heptane	5	16.5	-
Isopentane	10	8.5	9
Light naphtha	20	-	-
C ₄ fraction	3	3	3
Alkylate	-	-	28
Isooctane	-	-	50
Properties			
Octane number			
RON	98.7	98.5	98.8
MON	84.3	80.5	96.6
Sensitivity *1	14.4	18.0	2.2
Density (15°C)	0.7881	0.7880	0.7001
RVP (kg/cm ²)	0.570	0.480	0.630

*1 Sensitivity: difference between RON and MON (RON-MON)

Performance of each of these gasolines of inventive and comparative examples was evaluated, using an engine for WRC rally use shown in Table 2 and measuring spark ignition advance, output torque, power and the like at engine speeds of 3,600 to 4,400 rpm.

TABLE 2

Engine for WRC rally use	
Total displacement	2,000 cc
Equipment	turbo charger, intercooler, DOHC
Engine type	horizontal opposed type

Results of the performance evaluation are shown in Fig. 1 (A) and (B) as the difference in the power efficiency between the gasoline of the inventive example 1 or 2 and the gasoline of the comparative example. In this instance, the difference in the power efficiency was expressed as a value calculated by subtracting each evaluation result of the gasoline of the comparative example from that of the gasoline of the inventive example 1 or 2. In the figure, curve 1 shows the difference in the power efficiency between the

gasoline of the inventive example 1 and the gasoline of the comparative example, and curve 2 shows the difference between the gasoline of the inventive example 2 and the gasoline of the comparative example.

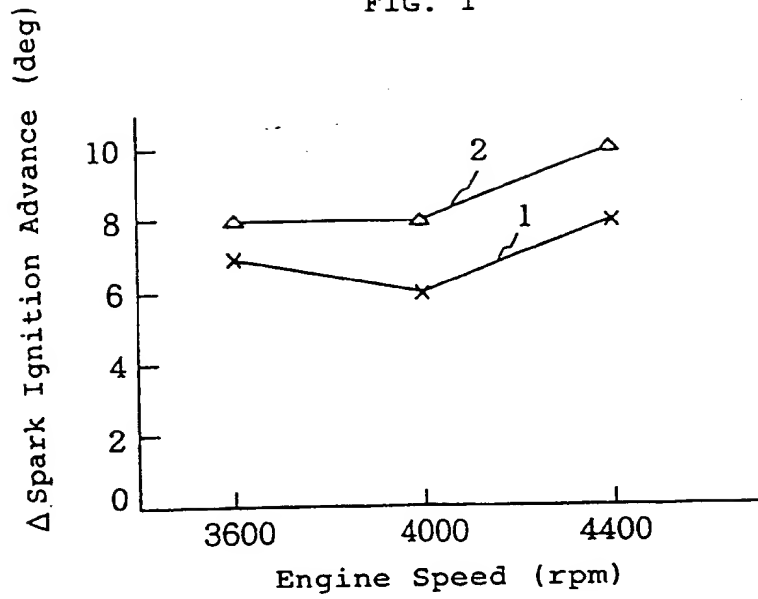
As shown in Fig. 1 (A), the difference in the spark ignition advance (Δ spark ignition advance, deg) between the gasoline of the inventive example 2 and the gasoline of the comparative example at engine speeds of 3,600 to 4,400 rpm reached 8 to 10. Also, as shown in Fig. 1 (B), the difference in the output torque (Δ output torque, kg/m) between the gasoline of the inventive example 2 and the gasoline of the comparative example at engine speeds of 3,600 to 4,400 rpm reached 9 to 11. Such an increased difference in the output torque is equivalent to a difference in the horse power of about 25 to 30 and therefore can be regarded as markedly great improvement in the engine power.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

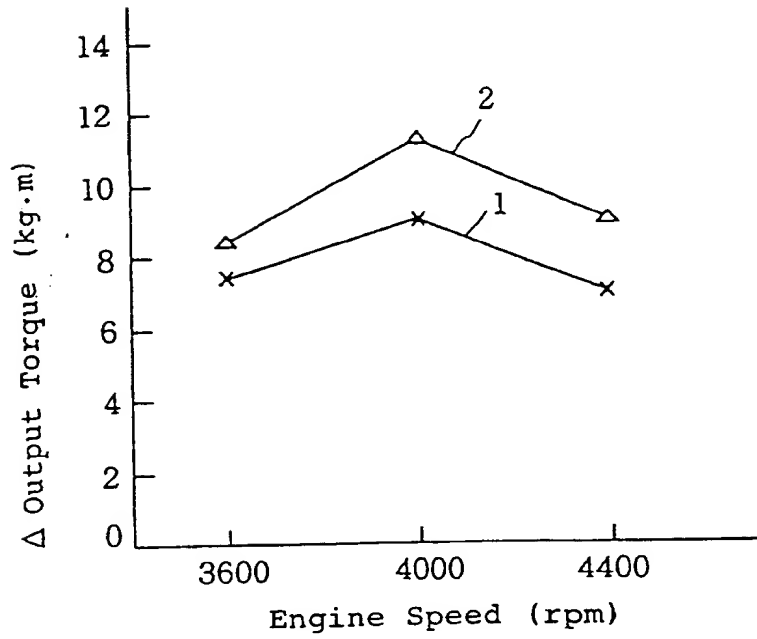
Claims

1. A lead-free high performance gasoline which contains toluene in an amount of from 50 to 70% by volume, n-heptane in an amount of from 2 to 10% by volume, isopentane in an amount of from 5 to 25% by volume and a C_4 fraction of distillate in an amount of from 2 to 5% by volume, wherein said lead-free high performance gasoline satisfies the conditions of density at $15^\circ\text{C} \leq 0.81 \text{ g/cm}^3$, $97 <$ research octane number ≤ 101 and Reid vapor pressure $\geq 0.4 \text{ kg/cm}^2$.
2. The lead-free high performance gasoline according to claim 1 wherein said gasoline further contains direct distillation light naphtha in an amount of from 10 to 30% by volume.
3. A lead-free high performance gasoline which contains toluene in an amount of from 45 to 60% by volume, methyl-tert-butyl ether in an amount of from 10 to 20% by volume, n-heptane in an amount of from 10 to 20% by volume, isopentane in an amount of from 5 to 15% by volume and a C_4 fraction of distillate in an amount of from 2 to 5% by volume, wherein said lead-free high performance gasoline satisfies the conditions of density at $15^\circ\text{C} \leq 0.81 \text{ g/cm}^3$, $97 <$ research octane number ≤ 101 and Reid vapor pressure $\geq 0.4 \text{ kg/cm}^2$.

FIG. 1



(A)



(B)



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 4918

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-5 004 850 (INTERSTATE CHEMICAL INC.) * claims 1,2,14,15,16,17,18 * ---	1,2	C10L1/06
A	US-A-4 812 146 (UNION OIL OF CALIFORNIA) * claims 1,2,3 * ---	1,2,3	
A	GB-A-630 245 (ANGLO IRANIAN OIL CO.) * claims 1,2 * ---	1	
A	DE-B-1 041 727 (DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) * claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08 DECEMBER 1992	Examiner OSWALD DE HERDT
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	